

sampling and testing the common carrier shall demonstrate evidence of an oversight program for monitoring compliance with the requirements of §80.1504 relating to the transport or storage of gasoline by tank truck, such as appropriate guidance to drivers on compliance with applicable requirements and the periodic review of records normally received in the ordinary course of business concerning gasoline quality and delivery.

(4) The periodic sampling and testing program specified in paragraph (b)(1) of this section shall be deemed to have been in effect during the relevant time period for any party, including branded gasoline refiners and branded gasoline importers, if:

(i) An EPA approved survey program under §80.1502 was in effect and was implemented fully and properly;

(ii) Any retailer at which a violation was discovered allowed survey inspectors to take samples and inspect labels; and

(iii) For truck loading terminals and truck distributors that perform oxygenate blending, additional quality assurance procedures and practices were in place, such as regular checks to reconcile volumes of ethanol in inventory and regular checks of equipment for proper ethanol blend rates.

§80.1508 What evidence may be used to determine compliance with the requirements of this subpart and liability for violations of this subpart?

(a) Compliance with the requirements of this subpart pertaining to the ethanol content of gasoline shall be determined based on the ethanol level of the gasoline, measured using the methodologies specified in §80.46(g). Any evidence or information, including the exclusive use of such evidence or information, may be used to establish the ethanol content of gasoline if the evidence or information is relevant to whether the ethanol content of gasoline would have been in compliance with the requirements of this subpart if the appropriate sampling and testing methodology had been correctly performed. Such evidence may be obtained from any source or location and may include, but is not limited to, test results using methods other than those

specified in §80.46(g), business records, and commercial documents.

(b) Determinations of compliance with the requirements of this subpart other than those pertaining to the ethanol content of gasoline, and determinations of liability for any violation of this subpart, may be based on information obtained from any source or location. Such information may include, but is not limited to, business records and commercial documents.

APPENDIX A TO PART 80—TEST FOR THE DETERMINATION OF PHOSPHORUS IN GASOLINE

1. Scope.

1.1 This method was developed for the determination of phosphorus generally present as pentavalent phosphate esters or salts, or both, in gasoline. This method is applicable for the determination of phosphorus in the range from 0.0008 to 0.15 g P/U.S. gal, or 0.2 to 49 mg P/liter.

2. Applicable documents.

2.1 ASTM Standards:

D 1100 Specification for Filter Paper for Use in Chemical Analysis.

3. Summary of method.

3.1 Organic matter in the sample is decomposed by ignition in the presence of zinc oxide. The residue is dissolved in sulfuric acid and reacted with ammonium molybdate and hydrazine sulfate. The absorbance of the "Molybdenum Blue" complex is proportional to the phosphorus concentration in the sample and is read at approximately 820 nm in a 5-cm cell.

4. Apparatus.

4.1 Buret, 10-ml capacity, 0.05-ml subdivisions.

4.2 Constant-Temperature Bath, equipped to hold several 100-ml volumetric flasks submerged to the mark. Bath must have a large enough reservoir or heat capacity to keep the temperature at 180 to 190 °F (82.2 to 87.8 °C) during the entire period of sample heating.

NOTE 1: If the temperature of the hot water bath drops below 180 °F (82.2 °C) the color development may not be complete.

4.3 Cooling Bath, equipped to hold several 100-ml volumetric flasks submerged to the mark in ice water.

4.4 Filter Paper, for quantitative analysis, Class G for fine precipitates as defined in Specification D 1100.

4.5 Ignition Dish—Coors porcelain evaporating dish, glazed inside and outside,

with pourout (size no. 00A, diameter 75 mm, capacity 70 ml).

4.6 Spectrophotometer, equipped with a tungsten lamp, a red-sensitive phototube capable of operating at 830 nm and with absorption cells that have a 5-cm light path.

4.7 Thermometer, range 50 to 220 °F (10 to 105 °C).

4.8 Volumetric Flask, 100-ml with ground-glass stopper.

4.9 Volumetric Flask, 1000-ml with ground-glass stopper.

4.10 Syringe, Luer-Lok, 10-ml equipped with 5-cm. 22-gage needle.

5. Reagents.

5.1 Purity of Reagents—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Purity of Water—Unless otherwise indicated, references to water shall be understood to mean distilled water or water of equal purity.

5.3 Ammonium Molybdate Solution—Using graduated cylinders for measurement add slowly (Note 2), with continuous stirring, 225 ml of concentrated sulfuric acid to 500 ml of water contained in a beaker placed in a bath of cold water. Cool to room temperature and add 20 g of ammonium molybdate tetrahydrate ($(\text{NH}_4)_6 \text{Mo}_7 \text{O}_{24} \cdot 4\text{H}_2\text{O}$). Stir until solution is complete and transfer to a 1000-ml flask. Dilute to the mark with water.

NOTE 2: Wear a face shield, rubber gloves, and a rubber apron when adding concentrated sulfuric acid to water.

5.4 Hydrazine Sulfate Solution—Dissolve 1.5 of hydrazine sulfate ($\text{H}_2 \text{NNH}_2 \cdot \text{H}_2 \text{SO}_4$) in 1 litre of water, measured with a graduated cylinder.

NOTE 3: This solution is not stable. Keep it tightly stoppered and in the dark. Prepare a fresh solution after 3 weeks.

5.5 Molybdate-Hydrazine Reagent—Pipet 25 ml of ammonium molybdate solution into a 100-ml volumetric flask containing approximately 50 ml of water, add by pipet 10 ml of $\text{N}_2 \text{NNH}_2 \cdot \text{H}_2 \text{SO}_4$ solution, and dilute to 100 ml with water.

NOTE 4: This reagent is unstable and should be used within about 4 h. Prepare it immediately before use. Each determination (including the blank) uses 50 ml.

5.6 Phosphorus, Standard Solution (10.0 µg P/ml)—Pipet 10 ml of stock standard phosphorus solution into a 1000-ml volumetric flask and dilute to the mark with water.

5.7 Phosphorus, Stock Standard Solution (1.00 mg P/ml)—Dry approximately 5 g of potassium dihydrogen phosphate ($\text{KH}_2 \text{PO}_4$) in an oven at 221 to 230 °F (105 to 110 °C) for 3 h. Dissolve 4.393 ± 0.002 g of the reagent in 150 ml, measured with a graduated cylinder, of $\text{H}_2 \text{SO}_4(1+10)$ contained in a 1000-ml volumetric flask. Dilute with water to the mark.

5.8 Sulfuric Acid (1+10)—Using graduated cylinders for measurement add slowly (Note 2), with continuous stirring, 100-ml of concentrated sulfuric acid ($\text{H}_2 \text{SO}_4$, sp gr 1.84) to 1 litre of water contained in a beaker placed in a bath of cold water.

5.9 Zinc Oxide.

NOTE 5: High-bulk density zinc oxide may cause spattering. Density of approximately 0.5 g/cm³ has been found satisfactory.

6. Calibration.

6.1 Transfer by buret, or a volumetric transfer pipet, 0.0, 0.5, 1.0, 1.5, 2.0, 3.0, 3.5, and 4.0 ml of phosphorus standard solution into 100-ml volumetric flasks.

6.2 Pipet 10 ml of $\text{H}_2 \text{SO}_4(1+10)$ into each flask. Mix immediately by swirling.

6.3 Prepare the molybdate-hydrazine solution. Prepare sufficient volume of reagent based on the number of samples being analyzed.

6.4 Pipet 50 ml of the molybdate-hydrazine solution to each volumetric flask. Mix immediately by swirling.

6.5 Dilute to 100 ml with water.

6.6 Mix well and place in the constant-temperature bath so that the contents of the flask are submerged below the level of the bath. Maintain bath temperature at 180 to 190 °F (82.2 to 87.8 °C) for 25 min (Note 1).

6.7 Transfer the flask to the cooling bath and cool the contents rapidly to room temperature. Do not allow the samples to cool more than 5 °F (2.8 °C) below room temperature.

NOTE 6: Place a chemically clean thermometer in one of the flasks to check the temperature.

6.8 After cooling the flasks to room temperature, remove them from the cooling water bath and allow them to stand for 10 min. at room temperature.

6.9 Using the 2.0-ml phosphorus standard in a 5-cm cell, determine the wavelength near 820 nm that gives maximum absorbance. The wavelength giving maximum absorbance should not exceed 830 nm.

6.9.1 Using a red-sensitive phototube and 5-cm cells, adjust the spectrophotometer to zero absorbance at the wavelength of maximum absorbance using distilled water in both cells. Use the wavelength of maximum absorbance in the determination of calibration readings and future sample readings.

6.9.2 The use of 1-cm cells for the higher concentrations is permissible.

6.10 Measure the absorbance of each calibration sample including the blank (0.0 ml phosphorus standard) at the wavelength of maximum absorbance with distilled water in the reference cell.

NOTE 7: Great care must be taken to avoid possible contamination. If the absorbance of the blank exceeds 0.04 (for 5-cm cell), check for source of contamination. It is suggested that the results be disregarded and the test be rerun with fresh reagents and clean glassware.

6.11 Correct the absorbance of each standard solution by subtracting the absorbance of the blank (0 ml phosphorus standard).

6.12 Prepare a calibration curve by plotting the corrected absorbance of each standard solution against micrograms of phosphorus. One millilitre of phosphorus standard solution provides 10 µg of phosphorus.

7. Sampling.

7.1 Selection of the size of the sample to be tested depends on the expected concentration of phosphorous in the sample. If a concentration of phosphorus is suspected to be less than 0.0038 g/gal (1.0 mg/litre), it will be necessary to use 10 ml of sample.

NOTE 8: Two grams of zinc oxide cannot absorb this volume of gasoline. Therefore the 10-ml sample is ignited in aliquots of 2 ml in the presence of 2 g of zinc oxide.

7.2 The following table serves as a guide for selecting sample size:

Phosphorus, milligrams per liter	Equivalent, grams per gallon	Sample size, milliliter
2.5 to 40	0.01 to 0.15	1.00
1.3 to 20	0.005 to 0.075	2.00
0.9 to 13	0.0037 to 0.05	3.00
1 or less	0.0038 or less	10.00

8. Procedure.

8.1 Transfer 2 ±0.2 g of zinc oxide into a conical pile in a clean, dry, unetched ignition dish.

NOTE 9: In order to obtain satisfactory accuracy with the small amounts of phosphorus involved, it is necessary to take extensive precautions in handling. The usual precautions of cleanliness, careful manipulation, and avoidance of contamination should be scrupulously observed; also, all glassware should be cleaned before use, with cleaning acid or by some procedure that does not involve use of commercial detergents. These compounds often contain alkali phosphates which are strongly adsorbed by glass surfaces and are not removed by ordinary rinsing. It is desirable to segregate a special stock of glassware for use only in the determination of phosphorus.

8.2 Make a deep depression in the center of the zinc oxide pile with a stirring rod.

8.3 Pipet the gasoline sample (Note 10) (see 7.2 for suggested sample volume) into the depression in the zinc oxide. Record the temperature of the fuel if the phosphorus content is required at 60 °F (15.6 °C) and make correction as directed in 9.2.

NOTE 10: For the 10-ml sample use multiple additions and a syringe. Hold the tip of the needle at approximately ¾ of the depth of the zinc oxide layer and slowly deliver 2 ml of the sample: fast sample delivery may give low results. Give sufficient time for the gasoline to be absorbed by the zinc oxide. Follow step 8.6. Cool the dish to room temperature. Repeat steps 8.3 and 8.6 until all the sample has been burned. Safety—cool the ignition dish before adding the additional aliquots of gasoline to avoid a flash fire.

8.4 Cover the sample with a small amount of fresh zinc oxide from reagent bottle (use the tip of a small spatula to deliver approximately 0.2 g). Tap the sides of the ignition dish to pack the zinc oxide.

8.5 Prepare the blank, using the same amount of zinc oxide in an ignition dish.

8.6 Ignite the gasoline, using the flame from a bunsen burner. Allow the gasoline to burn to extinction (NOTE 10).

8.7 Place the ignition dishes containing the sample and blank in a hot muffle furnace set at a temperature of 1150 to 1300 °F (621 to 704 °C) for 10 min. Remove and cool the ignition dishes. When cool gently tap the sides of the dish to loosen the zinc oxide. Again place the dishes in the muffle furnace for 5 min. Remove and cool the ignition dishes to room temperature. The above treatment is usually sufficient to burn the carbon. If the carbon is not completely burned off place the dish into the oven for further 5-min. periods.

NOTE 11: Step 8.7 may also be accomplished by heating the ignition dish with a Meker burner gradually increasing the intensity of heat until the carbon from the sides of the dish has been burned, then cool to room temperature.

8.8 Pipet 25 ml of H₂ SO₄ (1+10) to each ignition dish. While pipeting, carefully wash all traces of zinc oxide from the sides of the ignition dish.

8.9 Cover the ignition dish with a borosilicate watch glass and warm the ignition dish on a hot plate until the zinc oxide is completely dissolved.

8.10 Transfer the solution through filter paper to a 100-ml volumetric flask. Rinse the watch glass and the dish several times with distilled water (do not exceed 25 ml) and transfer the washings through the filter paper to the volumetric flask.

8.11 Prepare the molybdate-hydrazine solution.

8.12 Add 50 ml of the molybdate-hydrazine solution by pipet to each 100-ml volumetric flask. Mix immediately by swirling.

Pt. 80, App. B

8.13 Dilute to 100 ml with water and mix well. Remove stoppers from flasks after mixing.

8.14 Place the 100-ml flasks in the constant-temperature bath for 25 min. so that the contents of the flasks are below the liquid level of the bath. The temperature of the bath should be 180 to 190 °F (82.2 to 87.8 °C) (NOTE 1).

8.15 Transfer the 100-ml flasks to the cooling bath and cool the contents rapidly to room temperature (NOTE 6).

8.16 Allow the samples to stand at room temperature before measuring the absorbance.

NOTE 12: The color developed is stable for at least 4 h.

8.17 Set the spectrophotometer to the wavelength of maximum absorbance as determined in 6.9. Adjust the spectrophotometer to zero absorbance, using distilled water in both cells.

8.18 Measure the absorbance of the samples at the wavelength of maximum absorbance with distilled water in the reference cell.

8.19 Subtract the absorbance of the blank from the absorbance of each sample (NOTE 7).

8.20 Determine the micrograms of phosphorous in the sample, using the calibration curve from 6.12 and the corrected absorbance.

9. Calculations.

9.1 Calculate the milligrams of phosphorus per litre of sample as follows:

$P, \text{ mg/litre} = P/V$

where:

P = micrograms of phosphorus read from calibration curve, and

V = millilitres of gasoline sample.

To convert to grams of phosphorus per U.S. gallon of sample, multiply mg P/litre by 0.0038.

9.2 If the gasoline sample was taken at a temperature other than 60 °F (15.6 °C) make the following temperature correction:

$\text{mg P/litre at } 15.6 \text{ °C} = [\text{mg P/litre at } t] [1+0.001(t-15.6)]$

where:

t = observed temperature of the gasoline, °C.

9.3 Concentrations below 2.5 mg/litre or 0.01 g/gal should be reported to the nearest 0.01 mg/litre or 0.0001 g/U.S. gal.

9.3.1 For higher concentrations, report results to the nearest 1 mg P/litre or 0.005 g P/U.S. gal.

10. Precision.

10.1 The following criteria should be used for judging the acceptability of results (95 percent confidence):

10.2 Repeatability—Duplicate results by the same operator should be considered sus-

pect if they differ by more than the following amounts:

g P/U.S. gal (mg-P/litre)	Repeatability
0.0008 to 0.005 (0.2 to 1.3) ..	0.0002 g P/U.S. gal (0.05 mg P/litre).
0.005 to 0.15 (1.3 to 40)	7% of the mean.

10.3 Reproducibility—The results submitted by each of two laboratories should not be considered suspect unless they differ by more than the following amounts:

g P/U.S. gal (mg-P/litre)	Reproducibility
0.0008 to 0.005 (0.2 to 1.3) ..	0.0005 g P/U.S. gal (0.13 mg P/litre).
0.005 to 0.15 (1.3 to 40)	13% of the mean.

[39 FR 24891, July 8, 1974; 39 FR 25653, July 12, 1974]

APPENDIX B TO PART 80—TEST METHODS FOR LEAD IN GASOLINE

METHOD 1—STANDARD METHOD TEST FOR LEAD IN GASOLINE BY ATOMIC ABSORPTION SPECTROMETRY

1. Scope.

1.1. This method covers the determination of the total lead content of gasoline. The procedure's calibration range is 0.010 to 0.10 gram of lead/U.S. gal. Samples above this level should be diluted to fall within this range or a higher level calibration standard curve must be prepared. The higher level curve must be shown to be linear and measurement of lead at these levels must be shown to be accurate by the analysis of control samples at a higher level of alkyl lead content. The method compensates for variations in gasoline composition and is independent of lead alkyl type.

2. Summary of method.

2.1 The gasoline sample is diluted with methyl isobutyl ketone and the alkyl lead compounds are stabilized by reaction with iodine and a quarternary ammonium salt. The lead content of the sample is determined by atomic absorption flame spectrometry at 2833 Å, using standards prepared from reagent grade lead chloride. By the use of this treatment, all alkyl lead compounds give identical response.

3. Apparatus.

3.1 Atomic Absorption Spectrometer, capable of scale expansion and nebulizer adjustment, and equipped with a slot burner and premix chamber for use with an air-acetylene flame.

3.2 Volumetric Flasks, 50-ml, 100-ml, 250-ml, and one litre sizes.